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(54) Title: ANTIMICROBIAL POLYMERIC COATING

(57) Abstract

An antimicrobial film comprising an adherent, transparent, abrasion-resistant polymeric film which can release an effective antimicrobial concentration of protons [H+] upon contact with water to create an acidic antimicrobial environment in an environmental surface.

* See back of page

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ANTIMICROBIAL POLYMERIC COATING

Field of the Invention

The invention relates to an antimicrobial composition, particularly to liquid antimicrobial compositions that yield adherent, transparent, abrasion resistant polymeric films having effective, prolonged antimicrobial properties.

Background of the Invention

Studies have indicated that the contamination of both wet and dry household surfaces with potentially pathogenic bacteria is widespread. Following a study of bacterial flora in 200 homes, Scott et al., in J. Hyg. Camb., Vol. 89, 279 (1982), concluded that improved decontamination procedures are necessary, particularly at sites which are repeatedly wetted, such as the surfaces of sinks, toilets, draining boards, stoves, washing machines, and the like. However, controlled in-use tests employing dilute aqueous detergents at kitchen and bathroom sites achieve no observable reduction in microbial contamination, while application of aqueous hypochlorite and phenolic disinfectant compositions only produced a significant reduction in contamination levels for three to six hours. In their evaluation of disinfectants in the domestic environment, Scott et al., in J. Hyg. Camb., Vol. 92, 193 (1984), hypothesized that the rapid recontamination was due both to fresh contamination of surfaces, such as toilets, and to the local multiplication of residual colonies of bacteria at repeatedly wetted sites, such as sinks. We believe that such concerns are applicable to many household, institutional and industrial surfaces.

Compositions intended for the controlled release of a disinfectant from a film of stabilized hydrophilic polymer are disclosed in U.S. Patent No. 3,966,902. The polymer complex is stabilized as a metal complex by the addition of an inorganic aluminum, zirc nium or zinc salt, such as aluminum chloride hydrate, to the polymerization mixture.

The stabilization adjuvant is necessary because, upon contact with water, films of simple hydrogels become highly swollen and rapidly elute their additives. Furthermore, dry films, both simple and metal complexed hydrogels, do not adhere well to ceramic and other hard surfaces and can lose their adhesion completely when wetted.

Other antimicrobial agents have been combined with film-forming polymeric materials to accomplish various ends. For example, U.S. Patent No. 3,325,436 discloses bacteria resistant latexes that incorporate α, α'-azobis (chloroformamidine). Similarly, U.S. Patent No. 2,689,837 discloses polymeric vinyl halides having improved resistance to deterioration caused by fungal and bacterial attack, which incorporate copper 8-quinolinolate into the polymer. Also, U.S. Patent No. 3,577,566 discloses a spray-on bandage material using acrylate and methacrylate polymers that may contain germicides or fungicides.

Phenols and thiophenols are known antimicrobial agents that have been incorporated into polymeric compounds. U.S. Patent No. 2,875,097 discloses the incorporation of phenolic compounds into polymers comprising heterocyclic nitrogen compounds. These polymers are used to render fabrics resistant to fungi and insects.

U.S. Patent No. 2,873,263 discloses an antibacterial polymeric resin used for fabricating plastic articles. These resins are formed by polymerizing an unsaturated monomer, such as alkyl acrylate, in the presence of certain aromatic phenols or thiophenols.

These antimicrobial systems can provide adequate sanitization of many environmental surfaces. However, many consumers desire to have a system that can sanitize surfaces without the addition of any small molecule antimicrobial into the environment that can be thought to be potentially harmful. Therefore, a continuing need exists for an antimicrobial composition capable of forming a strong, small molecule antimicrobial free, polymeric film which provides rapid surfac kill of pathogenic bacteria and other

potentially harmful microorganisms. A need also exists for an antimicrobial polymeric film capable of providing a water-resistant surface with prolonged life and prolonged resistance to microbial growth.

Brief Description of the Invention

We have found new antimicrobial films that can be easily formed from a liquid composition. When applied to a target surface, the liquid film-forming composition yields a strongly antimicrobial polymeric film. The film protects the surface from microbial growth by forming an acidic, aqueous layer that can maintain a pH which can kill microbial growth and sanitize the treated surface.

We have found a vinyl polymer capable of sanitizing environmental surfaces in the absence of a small molecule antimicrobial. The polymer comprises repeating units derived from at least one monomer with a pendent acidic group having a pKa less than 3 or preferably less than 2. As used herein with respect to antimicrobial action or to the lifetime of the films of the invention, the term "prolonged" is intended to refer to retention of substantial antimicrobial action greater than 4 log reduction, preferably greater than 5 log reduction of microbial population as determined by laboratory test methods after 2 water washes and between a 4 log and a 3 log reduction after 2-10 water washes.

The polymer is typically applied as a liquid solution or dispersion in a suitable solvent or medium. An aqueous liquid can be used with the benefit that the polymer antimicrobial activity needs no activation because water in the film, when formed, can act to sanitize. Films cast from non-aqueous solution must be wet to create a sanitizing pH.

The antimicrobial film must comprise at least one monomer having a pendent acidic group with a pKa of less than 3 or preferably 2. The pendent acidic group may comprise a sulfonic acid group, a phosphoric or phosphonic acid group, a carboxylic acid group activated by a strong lectron withdrawing group, or any other p ndent groups acting as an

acid and capable of being incorporated into the polymer. Alternatively the acid group can be grafted onto a preformed polymer.

The polymer is substantially uncrosslinked, and the acid functional film may be dissolved or suspended in a suitable solvent or medium and the resulting solution used directly as a liquid sanitizing composition. The liquid composition may be applied to a surface by spraying, wiping, pouring and the like. The resultant films may be clear or opaque. The films strongly adhere to a multitude of surfaces and are resistant to abrasion.

Although not intending to be bound to any theory of action, the film appears to act as an antimicrobial agent by releasing an active antimicrobial concentration of protons [H+] when in contact with water. When the user wipes the film-treated surface with a damp cloth or sponge, the film is activated. Once the film is activated, a thin aqueous layer of a highly acidic nature creates an environment unsuitable for microorganisms to live or reproduce in. We have found that a certain mole fraction of monomer, with a carboxylic acid group having a pKa of < 3 or preferably < 2, reduces microbial populations by 5 orders of magnitude in as short a time as 15-30 minutes. The film may be reactivated many times by periodic wiping with a damp cloth or sponge or any other means designed to contact the surface with water.

Detailed Description of the Invention

A surface that is coated with an antimicrobial film of the invention will provide prolonged protection against microorganisms. Coatings of the instant antimicrobial composition can be applied to surfaces found in homes, hospitals, schools and the workplace. The films will be useful to combat diseases that can be spread by a wide variety of microorganisms.

The instant microbial composition may be applied to a surface in a number of ways. The films can be readily deposited from dilute aqueous solutions or dispersions of the copolymer in an aqueous solution. The compound can be

dissolved in a suitable solvent, preferably an organic solvent. The choice of solvents relates to desired rates of evaporation, of flammability concerns, toxicity concerns, etc. The preferred solvent is a water-alcohol mixture. The instant microbial composition can be applied to a surface by a number of methods including the wiping of the composition onto a surface with a cloth or sponge; pouring the composition onto a surface and spreading it with a mop, squeegee sponge, or cloth; dispensing the composition from a container equipped with a pump spray mechanism; dispensing the composition propelled by an aerosol from a suitable pressurized container; providing the composition in sufficient concentrations on a cloth or other absorbent carrier; and packaging the pre-moistened carriers for disposable uses and other methods capable of applying liquids to surfaces.

The film may be activated by contact with moisture from any means. Contact with atmospheric humidity can assist in maintaining treated surfaces in a substantially microbe-free condition, while exposure to larger amounts of water, as when the surface is moistened by wiping with a damp material, food residues, dishwater, and the like, can lead to the release of protons, creating an acidic environment. The polymeric films remain clear and non-tacky and, thus, do not detract from the appearance of the surfaces to which they are applied.

Hard surfaces suitable for coating the instant polymeric films include surfaces composed of refractory materials, such as glazed and unglazed tile, brick, porcelain, ceramics, metals, and glass; and hard plastics, such as formica, polystyrenes, vinyls, acrylics, polyesters, and the like.

The liquid composition is preferably coated at a thickness efficient to form a residual film of about 0.01-5 millimeters, with the most preferred being 0.5-1.0 millimeters.

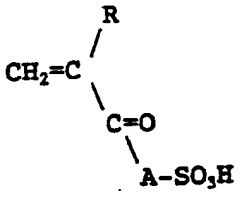
The antimicrobial polymer of the invention can be made in two primary alternative methods. The polymer can be formed from the mon mer having a p nd nt acid group with a pKa of

less than 3 or preferably less than 2. Alternatively, a preformed polymer molecule can have grafted onto the polymer chain a group containing the pendent acidic group having a pKa of less than 3.

Monomers that can be used either in the formation of the polymer chain or in the formation of an acidic group containing graft moiety include monomers having pendent acid functionality. The monomers of the invention are typically vinyl unsaturated monomers having an ethylenically unsaturated group connected to an acid group with a pKa of less than 3 through a linking moiety. The linking moiety can be formed from a large variety of well known and understood compositions including aromatic groups, aliphatic groups, quaternary amino groups, amide groups, polyether groups, saturated cyclic groups, ester groups, amine groups, etc.

The preferred pendent acidic functionality can be in the form of a sulfonic acid group, a phosphoric acid group, an activated phenolic group, an activated carboxylic acid group, or mixtures thereof. The phenolic and carboxylic acid groups are typically activated by the substitution of a strong electron withdrawing, or electronegative, group onto an atom positioned to activate either the phenolic (-OH) or the carboxylic acid group (-C(C=O)-OH). Such electron withdrawing groups are common halogen species including fluoride, chloride, bromide, iodine, nitro groups, methoxy groups, etc. Hydrogen and lower alkyls are not electron withdrawing groups.

Typical sulfonic acid containing monomers include vinyl aromatic sulfonic acids such as vinyl benzene sulfonic acid, vinyl benzyl sulfonic acid, etc.; acrylic monomers containing a sulfonic acid group according to the following formula:



wherein R comprises a hydrogen or a C_{1-5} alkyl group, and A comprises an alkylene group, a cyclic alkylene group, a phenyl group, or a group consisting of the following:

$$-O-(CH_2)n-$$

$$-NH-CH_2-$$

$$-NH-\overset{\overset{O}{\|}}{C}-CH_2-$$

$$-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-$$

$$-NH-\overset{\overset{O}{\|}}{C}-NH-CH_2-, \text{ etc.}$$

and others. The preferred sulfonic acid containing monomers comprise a hydrophilic acrylamido sulfonic acid or sulfonate monomer of the following formula:

$$CH_2=C(R')-\overset{\overset{O}{\|}}{C}-N(H)-R-SO_3H$$

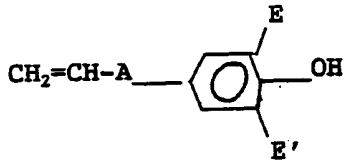
or salts thereof, wherein R is a straight or branched alkaline group of up to 10 carbon atoms, and R' is hydrogen or a C_{1-5} lower alkyl. The monomer can be used in the form of a sodium, potassium, ammonium or other salt of the sulfonic acid group. The most preferred sulfonic acid containing monomer comprises 2-acryloamido-2-methylpropane sulfonic acid (AMPS) having the following structural formula:

$$CH_2=CH-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-SO_3H$$

and sodium, potassium or ammonium salts thereof.

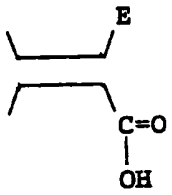
Phosphoric acid monomers comprise a class of monomers similar to the sulfonic acid monomers except that the monomers have phosphoric or phosphonic acid groups in place of the sulfonic acid group.

Active phenolic containing monomers are vinyl unsaturated monomers containing activated phenolic groups. Such monomers have formulas including:



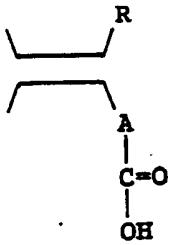
wherein E and E' are electron withdrawing groups and A is a linking group as set forth above for the acrylic monomers. Typical electron withdrawing groups include nitro, common halogens including chloride, fluoride, bromide, and iodide, alkoxy groups, etc.

The activated carboxylic acid monomers include vinyl unsaturated carboxylic acids having an electron withdrawing group in a position that can activate the carboxylic acid functionality. Typically the electron withdrawing group is positioned on an atom adjacent to the carboxylic acid group. Such monomers are typically represented by the following formula:



wherein E represents a common electron withdrawing group as set forth above.

Another activated carboxylic acid includes an electron withdrawing group immediately adjacent the carboxylic acid. The following monomer is illustrative:



Typically A is substituted with an electron withdrawing group and is a common C_{1-6} alkylene or cycloalkylene group. Preferred monomers include 2-chloropropeneoic acid, 2-fluoropropeneoic acid, 2-chlorobuteneoic acid, 2-fluorobuteneoic acid, 2-chloro-4-vinyl-cyclohexane carboxylic acid and others.

Homopolymer

The monomers described may be homopolymerized to form a film-forming polymer. The resultant film has prolonged antimicrobial properties. The homopolymer, as well as the copolymer and terpolymers described below, can be prepared by carrying out the polymerization of the monomers in a solvent or solvent mixture and at concentrations wherein the resultant polymers remain in solution. Preferred solvents include lower alkanols, such as ethanol; ketones, such as acetone, glycol esters or ethers; lower (alkyl) acetates; tetrahydrofuran; dimethylformamide; and the like. The monomeric starting materials are typically dissolved in a solvent to the desired concentration, e.g., to a total concentration of about 10 to 35% by weight, although somewhat higher or lower concentrations may be employed in some cases.

The polymerization reaction is initiated in a conventional manner, preferably by use of a catalytic amount of a suitable initiator. Examples of suitable initiators include 2,2'-azobis [2-methyl propionitrile] [AIBN], dibenzoyl peroxide, tert-butyl peroctoate, cumene hydroperoxide, diisopropyl percarbonate, ammonium persulfate, and the like, per se, or in combination with reducing agent in the form of an oxidation-reduction system.

During the course of the reaction, the reaction mixture may be agitated and heated, preferably under an inert atmosphere, to about 50 to 100°C, preferably to about 75-95°C After completion of the polymerization reaction, a solution of polymer results which can be applied to the target surface without further purification or concentration, or can be collected and redissolved in an ther s lvent.

Cop lym r

The monomers listed above may be copolymerized with alpha, beta-unsaturated carboxylic acids, such as methacrylic acid, acrylic acid, itaconic acid, aconitic acid, cinnamic acid, crotonic acid, mesaconic acid, maleic acid, fumaric acid, and the like. The preferred carboxylic acid comonomer is methacrylic acid.

In addition, the pendent acidic monomers may be copolymerized with alpha, beta-unsaturated carboxylic acid esters of the carboxylic acids described above. Such esters include aromatic esters, cycloakyl esters, alkyl esters, (hydroxy) alkyl esters, or (alkoxy) alkyl esters. The carboxylic acid ester comonomer typically is present in a concentration of about 5-60% by weight, and preferably about 10-45% by weight of the total polymer.

As used herein, the term "cycloalkyl ester" includes mono-, bi- and tricycloalkyl esters, and the term "aromatic ester" includes heteroaromatic esters. Especially preferred cycloalkyl and aromatic esters are those of acrylic acid, methacrylic acid, or itaconic acid. Useful aromatic esters of these acids include phenyl, benzyl, tolyl, tetrahydrofurfuryl, and phenoxyethyl esters. Useful cycloalkyl esters include (C_5-C_{12}) cycloalkyls, e.g., the cyclohexyl, cyclopentyl, isobornyl and adamantyl esters of these acids.

Preferred (hydroxy) alkyl ester comonomers include (2-hydroxyethyl) methacrylate, (2-hydroxyethyl) ethacrylate, (2-hydroxyethyl) acrylate, (3-hydroxypropyl) methacrylate, (3-hydroxypropyl) acrylate, or (3-hydroxy-propyl) ethacrylate.

Alkyl and (alkoxy) alkyl esters of alpha, beta-unsaturated carboxylic acids can be used in combination with the aromatic and/or cycloalkyl ester. Preferably, the alkyl esters will be selected from high alkyl esters, such as those of about 5-22 carbon atoms, most preferably about 7-12 carbon atoms.

The alkyl and (alkoxy) alkyl sters of acrylic acid, methacrylic acid and itaconic acid are preferred for use as comonomers.

Examples of useful (C_5-C_{12}) alkyl esters include: hexyl, octyl, ethyl(hexyl), isodecyl, and lauryl acrylates, methacrylates and itaconates. Examples of (alkoxy)alkyl esters useful as comonomers include (C_1-C_4) alkoxyl-(C_1-C_4)alkyl esters of acrylic, methacrylic or itaconic acids such as (methoxy) ethyl, (ethoxy) ethyl, (methoxy) propyl, (ethoxy) propyl, and the like.

Examples of suitable esters include: (2-hydroxyethyl)acrylate or methacrylate, (hydroxypropyl) acrylate or methacrylate, (dimethyl aminoethyl) methacrylate, (piperidinoethyl) methacrylate, (morpholino-ethyl) methacrylate, methacrylglycolic acid, the monomethacrylates of glycol, glycerol and other polyhydric alcohols, monomethacrylates of dialkylene glycols and polyalkylene glycols.

Alpha, beta-unsaturated amides may also be copolymerized with the aforementioned monomers, including acrylamide, methacrylamide, diacetone acrylamide, methylolacrylamide, methylolmethacrylamide, and the like.

Terpolymers

The monomers listed above with pendent acidic groups may be reacted with two different co-reactants to form a terpolymer which, when dissolved in a solvent and coated on a surface, forms an abrasion resistant polymeric film having prolonged antimicrobial properties. A preferred terpolymer of the present invention includes acrylamido-2-methylpropane sulfonic acid, ethylmethacrylate and hydroxyethyl methacrylate. Ratios of the monomers of the terpolymer acrylamidopropanesulfonic acid, ethylmethacrylate, hydroxymethylmethacrylate range from 1-2, 1-7, 1-4, respectively. It has been found that the use of hydroxyethylmethacrylate improves the film properties such as adhesion and durability of the antimicrobial film.

Other terpolymers include the use of hydroxy ethyl methacrylate and ethyl methacrylate in conjunction with other monomers such as itaconic acid, acrylic acid, styrene sulfonic acid, styrene phosphonic acid, chloroacrylic acid, bromoacrylic acid, and cyanoacrylic acid.

The monomers listed above may be copolymerized with alpha, beta-unsaturated carboxylic acids, such as methacrylic acid, aconitic acid, cinnemic acid, crotonic acid, mesaconic acid, maleic acid, fumaric acid, and the like. The preferred carboxylic acid termonomer is methacrylic acid.

In addition, the pendent acidic monomers may be terpolymerized with alpha, beta-unsaturated carboxylic acid esters of the carboxylic acids described above. Such esters include aromatic esters, cycloalkyl esters, alkyl esters, (hydroxy)alkyl esters, or (alkoxy)alkyl esters.

Preferred cycloalkyl and aromatic esters are those of acrylic acid, methacrylic acid, or itaconic acid. Useful aromatic esters of these acids include phenol, benzyl, tolyl, tetrahydrofurfuryl, and phenoxyethyl esters. Useful cycloalkyl esters include (C_5-C_{12}) cycloalkyls, e.g., the cyclohexyl, cyclopentyl, isobornyl and adamantyl esters of these acids.

Preferred (hydroxy)alkyl ester comonomers include (2-hydroxyethyl) methacrylate, (2-hydroxyethyl) and (ethacrylate, (2-hydroxyethyl) acrylate, (3-hydroxy- propyl) methacrylate, (3-hydroxypropyl) acrylate, or (3-hydroxypropyl) ethacrylate.

Alkyl and (alkoxy) alkyl esters of alpha, beta-unsaturated carboxylic acids can be used in combination with the aromatic and/or cycloalkyl ester. Preferably, the alkyl esters will be selected from high alkyl esters, such as those of about 5-22 carbon atoms, most preferably, about 7-12 carbon atoms.

Examples of useful (C_5-C_{12}) alkyl esters include: hexyl, octyl, ethyl(hexyl), isodecyl, and lauryl acrylates, methacrylates and itaconates. Examples of (alkoxy)alkyl sters useful as comonomers includ : (C_1-C_4)

alkoxyl-(C_1-C_4)alkyl esters of acrylic, methacrylic or itaconic acids such as (methoxy) ethyl, (ethoxy) ethyl, (methoxy) propyl, (ethoxy) propyl, and the like.

Examples of suitable esters include: (2-hydroxyethyl) acrylate or methacrylate, (hydroxypropyl) acrylate or methacrylate, (dimethylaminoethyl) methacrylate, (piperidinoethyl) methacrylate, (morpholinoethyl) methacrylate, methacrylglycolic acid, the monomethacrylates of glycol, glycerol and other polyhydric alcohols, monomethacrylates of dialkylene glycols and polyalkylene glycols.

Alpha, beta-unsatured amides may also be terpolymerized with the aforementioned monomers, including acrylamide, methacrylamide, diacetone acrylamide, methylolacrylamide, methylolmethacrylamide, and the like.

Synthesis

The polymers, copolymers and terpolymers of this invention can be produced using conventional polymerization techniques including bulk, solution, suspension, or other polymerization techniques. Typically the polymers and copolymers of the invention can easily be prepared by polymerizing the selected monomers and typically alcoholic solvents at elevated temperature using free radical, redox or other catalysis. Once polymerization is complete, the polymer can be removed from the reaction medium by removing the volatile solvent, precipitation, dialysis, or other typical purification technique.

Example I

Into a 3 neck round bottom flask were added 28.4 ml of ethyl alcohol, 3.11 grams of 2-acrylamido-2-methylpropane sulfonic acid and 3.99 grams of ethyl methacrylate. The mixture was stirred under nitrogen at room temperature until all of the solid dissolved. Upon dissolution, 0.0355 grams of 2,2'-azobis(2-methylpropionitrile) was added and the temperature of the solution was raised at 75°C The mixture remain d at 75°C for 5 hours and was allow d to cool th reaft r. Th soluti n was then poured into a flask

containing 200 ml of ether. A white precipitate was formed which was dried in a vacuum oven at 50°C for 12 hours. The yield of the copolymer was 61%.

Examples II-V

Examples II-V were prepared following the procedure of Example I except that the mole ratio of ethyl methacrylate (EMA) to 2-acrylamide-2,2-methylpropanesulfonic acid (AMPS) is reduced by 10 mole-% in the Examples.

Polymer Example I-(EMA/AMPS)=1:1

Polymer Example II-(EMA/AMPS)=3:2

Polymer Example III-(EMA/AMPS)=7:3

Polymer Example IV-(EMA/AMPS)=4:1

Polymer Example V-(EMA/AMPS)=9:1

Example VI

Into a 3 neck round bottom flask was added 27 ml of isopropanol, 2.07 grams of 2-acrylamido-2-methylpropane sulfonic acid, 0.65 grams of 2-hydroxyethylmethacrylate (HEMA) and 3.99 grams of ethyl methacrylate. The solution was stirred under nitrogen at ambient temperature. One ml of water was then added to the solution which was heated to 45°C to dissolve all of the solid. Then 0.0336 grams of 2,2'-azobis(2-methylpropionitrile) was added and the temperature was raised to 83°C to commence the polymerization. The solution was refluxed for 5 hours, after which the solution was cooled to room temperature. The solution was then poured into a 100 ml ether/100 ml hexane mixture. A white precipitate appeared which was washed twice with hexane and dried in a vacuum oven at 53°C for 12 hours. The yield of the terpolymer was 81%.

Examples VII-XIII

Examples VII-XIII were made using the procedure of Example VI with the following mole ratios.

Polymer Example VII - (EMA/HEMA/AMPS) = 1:1:1

Polymer Example VIII - (EMA/HEMA/AMPS) = 4:4:2

Polymer Example IX - (EMA/HEMA/AMPS) = 6:2:2

Polymer Example X - (EMA/HEMA/AMPS) = 7:1:2

Polymer Example XI - (EMA/HEMA/AMPS) = 15:1:4

Polymer Example XII - (EMA/HEMA/AMPS) = 15:2:3
Polymer Example XIII - (EMA/HEMA/AMPS) = 16:1:3

Example XIV

Into a 3 neck round bottom flask were added 18.0 ml of isopropyl alcohol, 2.66 grams (25 mmole) of α-chloroacrylic acid and 3.25 grams (25 mmole) of 2-hydroxyethyl methacrylate. A reaction was initiated in the flask under nitrogen by 29.6 ml of AIBN (azobisisobutyronitrile). The reaction was refluxed at 86°C for two hours. The mixture was then allowed to cool, and thereafter poured into 200 ml of ethyl ether while stirring. A white precipitate formed. The solvent was decanted and the precipitate was collected, washed and dried in a vacuum oven at room temperature overnight. The yield was 85% of a copolymer of α-chloroacrylic acid and 2-hydroxyethyl methacrylate.

Example XV

Into a 3 neck round bottom flask were added 22.2 ml of isopropyl alcohol, 3.73 grams (35 mmole) of α-chloroacrylic acid, (ClAA) 0.65 grams (5 mmole) α-hydroxy ethyl methacrylate and 1.14 grams (10 mmole) ethyl methacrylate. A reaction was initiated in the flask under nitrogen by 27.6 mg of Azobisiso butyronitrile (AIBN). The reaction was refluxed at 86°C for two hours. The mixture was then allowed to cool, and thereafter poured into 200 ml of ethyl ether while stirring. A white precipitate was formed. The solvent was decanted and the precipitate was collected/washed and dried in a vacuum oven at room temperature overnight. The yield was 85% of a terpolymer of α-chloroacrylic acid, 2-hydroxyethyl methacrylate and ethyl methacrylate.

Example XVI - XVIII

Examples XVI-XVIII were prepared following the same procedure as Example XV except the mole ratios were as follows:

Polymer Example XVI - (ClAA/HEMA/EMA)=1/1/1
Polymer Example XVII - (ClAA/HEMA/EMA)=3/1/6
Polymer Exampl XVIII - (ClAA/HEMA/EMA)=5/1/4

Microbiological Testing

Polymeric films for microbiological testing were prepared as follows: 200 milligrams of polymer was dissolved in 4 milliliters of acetone. The solution was poured into 100 x 15 mm glass petri dish. The solvent was evaporated in a hood at 25°C.

The film was inoculated as follows: Cells of a 24-hour culture of gram positive Staphylococcus aureus were spun down in a centrifuge and then re-suspended in deionized water. A 0.1 milliliter inoculum of the suspension were spread onto the film. The dish was covered and stored in a humidity chamber to prevent drying of the inoculum.

After incubation at 25°C, 90-95% humidity, the film was swabbed with a 1 x 1 inch wet cotton swatch which was then added to 9 milliliters of a neutralizer solution (0.1 M Na-K phosphate buffer, pH 7.2) and vortexed. The solution was appropriately diluted and plated out using Tryptone-Glucose-Yeast extract agar (Difco Inc.). The control was an empty glass petri dish without the film. The results are described in Tables 1 and 2 below.

TABLE 1

ANTI-MICROBIAL ACTIVITY

	Log (base 10) Reductions				
Contact Time (Min.)	1	15	30	60	240
Polymer					
Ex. I (EMA/50% AMPS)	4.36	>6.6	>6.6	>6.6	>6.6
Ex. II (EMA/40% AMPS)	2.95	>6.6	>6.6	>6.6	>6.6
Ex. III (EMA/30% AMPS)	2.46	>6.6	>6.6	>6.6	>6.6
Ex. IV (EMA/20% AMPS)	1.97	>6.6	>6.6	>6.6	>6.6
Ex. V (EMA/10% AMPS)	0.46	>6.6	>6.6	>6.6	>6.6

TABLE 2

ANTI-MICROBIAL ACTIVITY

	Log (base 10) Reductions				
Contact Time (Min.)	1	15	30	60	240
Polymer (EMA/HEMA/AMPS)					
Ex. VII (1/1/1)	3.8	6.8	6.8	6.8	6.8
Ex. VIII (4/4/2)	2.6	4.8	5.9	6.8	6.8
Ex. IX (6/2/2)	2.6	4.5	5.4	6.8	6.8
Ex. X (7/1/2)	2.6	6.8	5.8	6.8	6.8
Ex. XI (15/1/4)	1.4	5.1	5.4	6.8	6.8
Ex. XII (15/2/3)	0.6	2.4	3.9	5.0	6.8
Ex. XIII (16/1/3)	0.8	0.8	3.2	4.7	6.8

TABLE 3

ANTI-MICROBIAL ACTIVITY

	Log (base 10) Reductions				
Contact Time (Min.)	1	15	30	60	240
Polymer					
Ex XIV (ClAA/HEMA=1:1)	1.9	4.4	6.0	>7.1	>7.1
Ex. XV (ClAA/ HEMA/EMA=7:1:2)	0.82	3.7	6.1	>7.1	>7.1
Ex. XVI (ClAA/ HEMA/EMA=3:1:6)	0.24	0.27	0.34	0.37	1.2
Ex. XVIII (ClAA/HEMA/ EMA=5:1:4)	0.37	0.66	0.75	0.95	2.9

The results show that since AMPS has a much lower pKa than α-chloroacrylic acid (pKa -1.2 vs. pKa 2.8), much less of it is needed to achieve the same degree of kill. In general, it was found that the pH on the surface of a wetted film has to be < 1 in order to obtain complete kill in 30 minutes.

Microbiological testing was repeated with the gram-negative organism Enterobacter aerogenes in place of S. aureus. Results are given in the following table.

TABLE 4

ANTI-MICROBIAL ACTIVITY

	Log (base 10) Reductions				
Contact Time (Min.)	1	15	30	60	240
Polymer					
Ex. VII (EMA/HEMA/AMPS=1:1:1)	2.4	>7.1	>7.1	>7.1	>7.1
Ex. VIII (EMA/HEMA/AMPS=4:4:2)	1.1	>7.1	>7.1	>7.1	>7.1
Ex. IX (EMA/HEMA/AMPS=6:2:2)	1.3	>7.1	>7.1	>7.1	>7.1
Ex. X (EMA/HEMA/AMPS=7:1:2)	0.98	>7.1	>7.1	>7.1	>7.1
Ex. XI (EMA/HEMA/AMPS=75:5:20)	1.03	>7.1	>7.1	>7.1	>7.1
Ex. XII (EMA/HEMA/ AMPS=75:10:15)	0.51	3.4	>7.1	>7.1	>7.1
Ex. XIII (EMA/HEMA/AMPS=80:5:15)	0.52	4.8	>7.1	>7.1	>7.1
Ex. XV (ClAA/HEMA/EMA=7:1:2)	0.16	3.5	>7.1	>7.1	>7.1
Ex. XVI (ClAA/HEMA/EMA=1:1)	0.34	7.1	>7.1	>7.1	>7.1

The results show that the films are more effective against E. aerogenes than S. aureus.

The invention can be understood and practiced from the description, examples and data set forth above. However a variety of embodiments of the invention can be made without departing from the spirit and scope of the invention. Accordingly, the invention resides in the claims hereinafter appended.

WHAT IS CLAIMED IS:

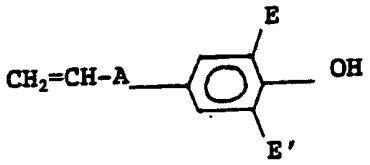
1. A vinyl polymer film capable of antimicrobial action on environmental surfaces, the vinyl polymer comprising repeating units derived from a monomer with a pendent acidic group having a pKa less than 3, wherein the polymer film is free of a small molecule antimicrobial.

2. The film of claim 1 wherein the monomer comprises a vinyl monomer having a pendent sulfonic acid group.

3. The film of claim 2 wherein the monomer comprises 2-acrylamido-2-methylpropane sulfonic acid.

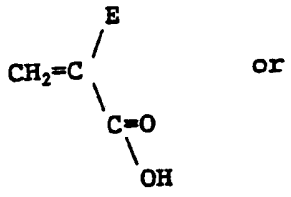
4. The film of claim 1 wherein the monomer comprises a vinyl monomer having a pendent phosphonic acid group.

5. The film of claim 1 wherein the monomer comprises a vinyl monomer having a pendent activated phenol group according to the formula:

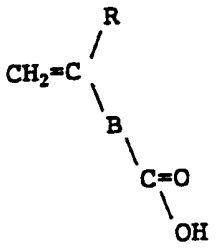


wherein E is an electron withdrawing group and A is a linking moiety.

6. The film of claim 1 wherein the monomer comprises an activated vinyl carboxylic acid monomer having the following formula:



or



wherein E is an electron withdrawing group, R is a C_{1-5} alkyl and B is a linking moiety having an electron withdrawing group activating the carboxylic acid group.

7. Th film of claim 1 wherein the vinyl polymer comprises a copolymer of a monomer having an acid group with a pKa of 1 ss than about 3 and an acrylic monomer.

8. The film of claim 7 wherein the acrylic monomer comprises an alkylacrylate, an alkylmethacrylate, a hydroxyalkylacrylate or a hydroxyalkylmethacrylate.

9. The film of claim 1 wherein the polymer comprises a copolymer of ethylmethacrylate and 2-acrylamido-2-methylpropane sulfonic acid.

10. The film of claim 1 wherein the polymer comprises a terpolymer of ethylmethacrylate, hydroxyethylmethacrylate, and 2-acrylamido-2-methylpropane propane sulfonic acid.

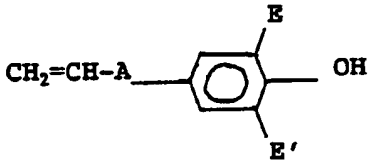
11. An aqueous antimicrobial composition capable of providing antimicrobial action on environmental surfaces in the substantial absence of a small molecule antimicrobial comprising a major proportion of an aqueous medium and a film-forming vinyl polymer comprising repeating units derived from a monomer with a pendent acidic group having a pKa less than about 3.

12. The film of claim 11 wherein the monomer comprises a vinyl sulfonic acid containing monomer.

13. The film of claim 12 wherein the vinyl sulfonic acid containing monomer comprises 2-acrylamido-2-methylpropane sulfonic acid.

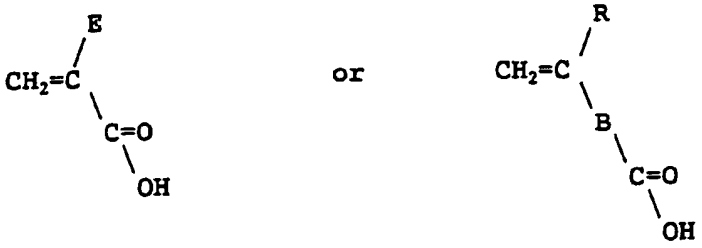
14. The film of claim 11 wherein the monomer comprises a vinyl phosphonic acid containing monomer.

15. The film of claim 11 wherein the monomer comprises a vinyl activated phenol monomer according to the formula:



wherein E is an electron withdrawing group.

16. The film of claim 11 wherein the monomer comprises an activated vinyl carboxylic acid monomer having the following formula:



wherein E is an electron withdrawing group, R is a C_{1-5} alkyl and B is a linking moiety having an electron withdrawing group activating the carboxylic acid group.

17. The film of claim 11 wherein the vinyl polymer comprises a copolymer of a monomer having an acid group with a pKa of less than about 3 and an acrylic monomer.

18. The film of claim 17 wherein the acrylic monomer comprises an alkylacrylate, an alkylmethacrylate, a hydroxyalkylacrylate, a hydroxyalkylmethacrylate, itaconic acid, maleic acid, or mixtures thereof.

19. The film of claim 11 wherein the polymer comprises a copolymer of ethylmethacrylate and acrylamido-2-methylpropane sulfonic acid.

20. The film of claim 11 wherein the polymer comprises a terpolymer of ethylmethacrylate, hydroxyethylmethacrylate, and 2-acrylamido-2-methylpropane sulfonic acid.

21. An aqueous antimicrobial composition capable of providing antimicrobial action on environmental surfaces in substantial absence of small molecule antimicrobials comprising a major proportion of an aqueous medium and a substantially uncrosslinked film-forming vinyl polymer comprising repeating units derived from 2-acrylamido-2-methylpropane sulfonic acid.

22. An aqueous antimicrobial composition capable of providing antimicrobial action on environmental surfaces in substantial absence of small molecule antimicrobials, comprising a major proportion of an aqueous medium and a substantially uncrosslinked film-forming vinyl polymer comprising a copolymer deriv d from thylmethacrylate and 2-acrylamido-2-methylpropane sulfonic acid.

23. An aqueous antimicrobial composition capable of providing antimicrobial action on environmental surfaces in substantial absence of small molecule antimicrobials, comprising a major proportion of an aqueous medium and a substantially uncrosslinked film-forming vinyl polymer comprising ethylenemethacrylate, hydroxyethylmethacrylate and 2-acrylamido-2-methylpropane sulfonic acid.

AMENDED CLAIMS

[received by the International Bureau on 17 January 1991 (19.01.91); original claims 1 and 11 amended; other claims unchanged (2 pages)]

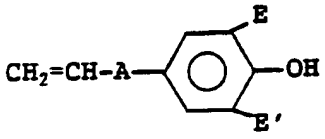
1. A vinyl polymer film capable of antimicrobial action on environmental surfaces, substantially uncrosslinked, film-forming vinyl polymer comprising repeating units derived from a monomer with a pendent acidic group having a pKa less than 3, wherein the polymer film is free of a small molecule antimicrobial.

2. The film of claim 1 wherein the monomer comprises a vinyl monomer having a pendent sulfonic acid group.

3. The film of claim 2 wherein the monomer comprises 2-acrylamido-2-methyl propane sulfonic acid.

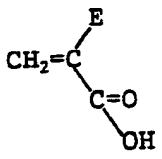
4. The film of claim 1 wherein the monomer comprises a vinyl monomer having a pendent phosphonic acid group.

5. The film of claim 1 wherein the monomer comprises a vinyl monomer having a pendent activated phenol group according to the formula:

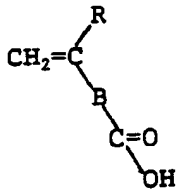


wherein E is an electron withdrawing group and A is a linking moety.

6. The film of claim 1 wherein the monomer comprises an activated vinyl carboxylic acid monomer having the following formula:



or



wherein E is an electron withdrawing group, R is a C_{1-5} alkyl and B is a linking moiety having an electron withdrawing group activating th carboxylic acid group.

7. Th film of claim 1 wherein the vinyl polymer comprises a copolymer of a monom r having an acid group

with a pKa of l ss than about 3 and an acrylic monomer.

8. The film of claim 7 wherein the acrylic monomer comprises an alkylacrylate, an alkylmethacrylate, a hydroxyalkylacrylate or a hydroxyalkylmethacrylate.

9. The film of claim 1 wherein the polymer comprises a copolymer of ethylmethacrylate and 2-acrylamido-2-methylpropane sulfonic acid.

10. The film of claim 1 wherein the polymer comprises a terpolymer of ethylmethacrylate, hydroxyethylmethacrylate, and 2-acrylamido-2-methylpropane propane sulfonic acid.

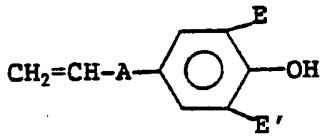
11. An aqueous antimicrobial composition capable of providing antimicrobial action on environmental surfaces in the substantial absence of a small molecule antimicrobial comprising a major proportion of an aqueous medium and a substantially uncrosslinked, film-forming vinyl polymer comprising repeating units derived from a monomer with a pendent acidic group having a pKa less than about 3.

12. The film of claim 11 wherein the monomer comprises a vinyl sulfonic acid containing monomer.

13. The film of claim 12 wherein the vinyl sulfonic acid containing monomer comprises 2-acrylamido-2-methylpropane sulfonic acid.

14. The film of claim 11 wherein the monomer comprises a vinyl phosphonic acid containing monomer.

15. The film of claim 11 wherein the monomer comprises a vinyl activated phenol monomer according to the formula:



wherein E is an electron withdrawing group.

16. The film of claim 11 wherein the monomer comprises an activated vinyl carboxylic acid monomer having the following formula:

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/03922

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: A 01 N 25/24, 25/10, 41/04

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	A 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4536206 (YOSHIAKI KUBO et al.) 20 August 1985 see claims 1-8,11 --	11,16-18
A	FR, A, 2476441 (MARUZEN OIL CO. LTD) 28 August 1981 . see claims --------	1-23

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
9th October 1990	08. 11. 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Mme N. KUIPER

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9003922 SA 38891

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/10/90 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4536206	20-08-85	JP-A- 59070601	21-04-84
FR-A- 2476441	28-08-81	JP-A- 56120601	22-09-81
		DE-A- 3107578	24-12-81
		GB-A,B 2072508	07-10-81